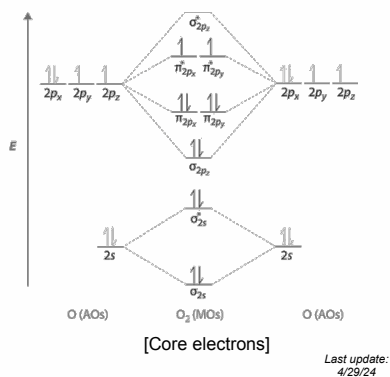


Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals

Chapter 8

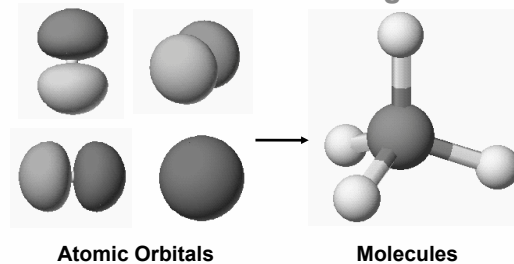
Chemistry 222
Professor Michael Russell

MAR



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Advanced Theories of Chemical Bonding



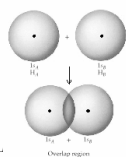
Two Theories of Bonding

VALENCE BOND (VB) THEORY - Linus Pauling

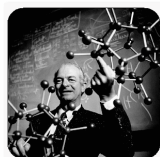
valence electrons are *localized* between atoms (or are lone pairs)

half-filled atomic orbitals overlap to form bonds.

electrons stabilized by 2 nuclei

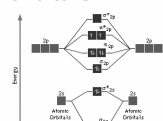


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MOLECULAR ORBITAL (MO) THEORY - Robert Mulliken

valence electrons are *delocalized* over entire molecule in molecular orbitals

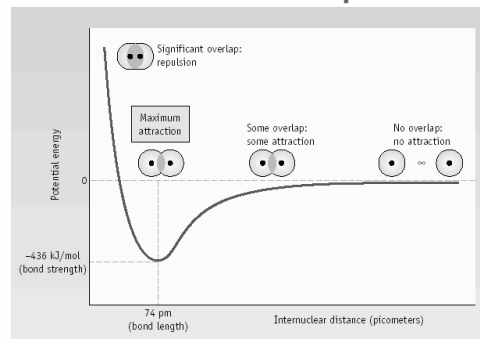


Robert Mulliken

MAR

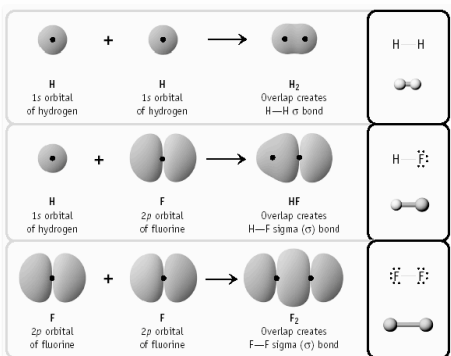
Sigma Bond Formation by Orbital Overlap

Two s orbitals overlap



Sigma Bond Formation by Orbital Overlap

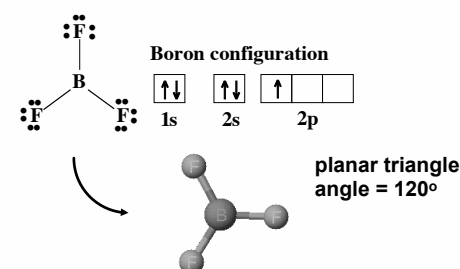
Two s orbitals overlap



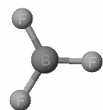
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Using Valence Bond Theory

Bonding in BF_3



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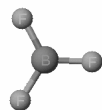
Bonding in BF₃

How to account for 3 bonds 120° apart using a spherical s orbital and p orbitals that are 90° apart?

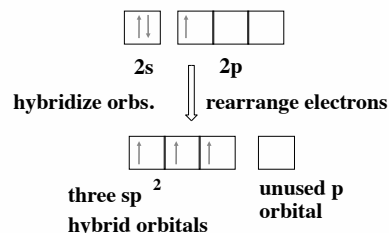
Pauling said to modify VB approach with **ORBITAL HYBRIDIZATION**

- mix available orbitals to form a new set of orbitals - **HYBRID ORBITALS** - that will give the maximum overlap in the correct geometry.

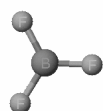
MAR



Bonding in BF₃

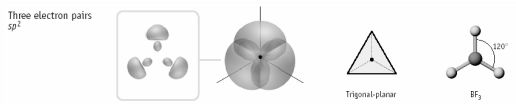


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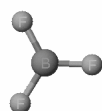
Bonding in BF₃

The three hybrid orbitals are made from 1 s orbital and 2 p orbitals create 3 sp² hybrids.

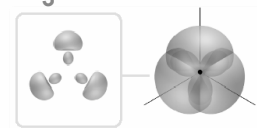
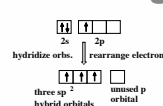


Now we have 3, half-filled **HYBRID** orbitals that can be used to form *planar* B-F sigma bonds.

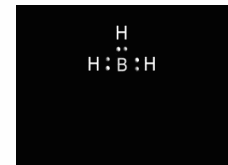
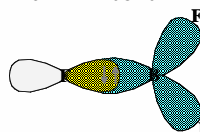
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Bonding in BF₃



An orbital from each F overlaps one of the sp² hybrids to form a B-F σ bond.

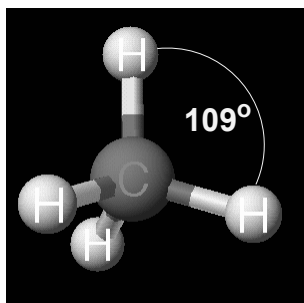


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Bonding in CH₄

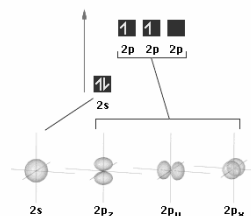
How do we account for 4 C-H sigma bonds 109° apart?

Need to use 4 atomic orbitals - s, p_x, p_y, and p_z - to form 4 new hybrid orbitals pointing in the correct direction.



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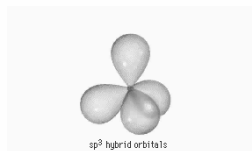
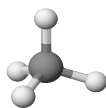
Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



4 C atom orbitals hybridize to form four equivalent sp³ hybrid atomic orbitals.

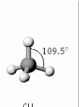
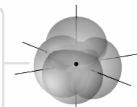
MAR

Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



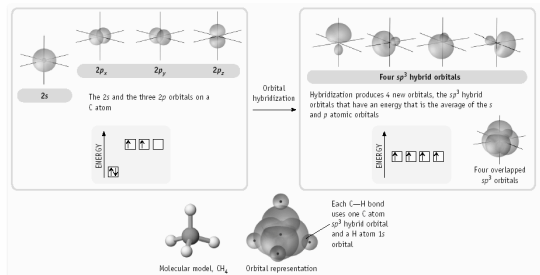
4 C atom orbitals hybridize to form four equivalent sp³ hybrid atomic orbitals.

Four electron pairs sp³



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Bonding in CH₄



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Orbital Hybridization

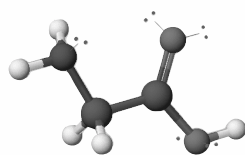
Bonds	EPG	Hybrid	REMAINING p orbs?
2	linear	sp	2 p
3	trigonal planar	sp ²	1 p
4	tetrahedral	sp ³	none
5	trigonal bipyramid	sp ³ d	---
6	octahedral	sp ³ d ²	---

see: VSEPR Guide

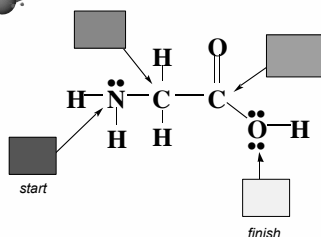
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	Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs sp		Linear	BeCl ₂ (180°)
Three electron pairs sp ²		Trigonal-planar	BF ₃ (120°)
Four electron pairs sp ³		Tetrahedral	CH ₄ (109.5°)

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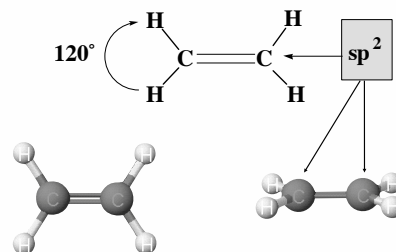
Bonding in Glycine



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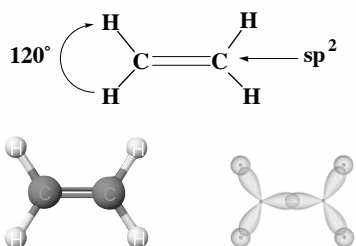
Multiple Bonds

Consider ethylene, C₂H₄



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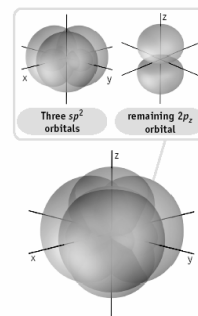
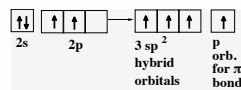
Sigma Bonds in C₂H₄



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π Bonding in C₂H₄

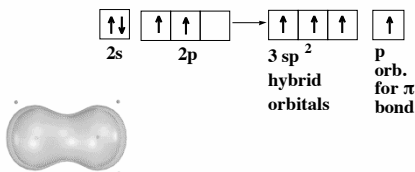
The unused p orbital on each C atom contains an electron and this p orbital overlaps the p orbital on the neighboring atom to form the π bond.



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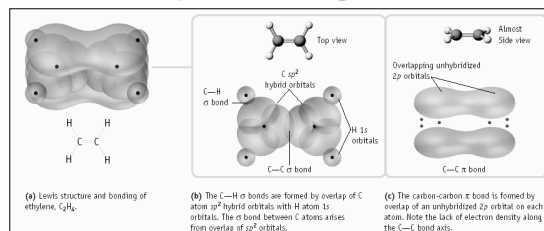
π Bonding in C₂H₄

The unused p orbital on each C atom contains an electron, and this p orbital overlaps the p orbital on the neighboring atom to form the π bond.



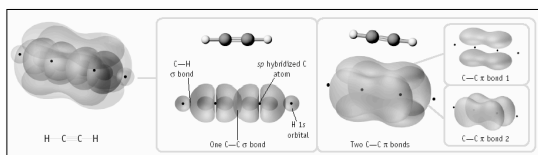
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Multiple Bonding in C₂H₄



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σ and π Bonding in C₂H₂

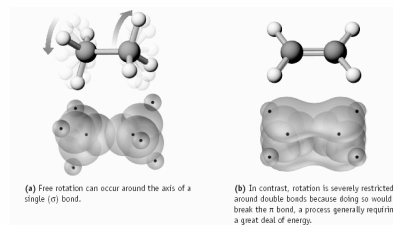


C₂H₂ has a triple bond

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Consequences of Multiple Bonding

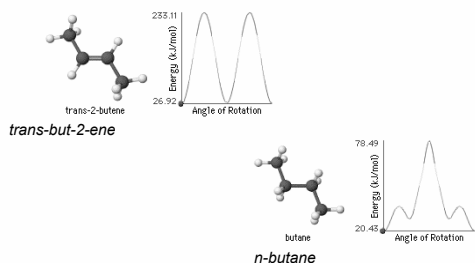
There is restricted rotation around C=C bond.



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Consequences of Multiple Bonding

Restricted rotation around C=C bond.

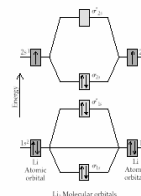


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Molecular Orbital Theory

- Accounts for paramagnetism, color, bonding
- Atomic orbitals delocalize into molecular orbitals
- Bonding, Antibonding and Nonbonding orbitals
- Quite complicated, need computers; we will only look at diatomics (2 atom systems) from the first and second periods only



Advantages of MO Theory



Dioxygen should be electron paired (*diamagnetic*) by VB Theory, but dioxygen is actually *paramagnetic*. MO Theory accounts for paramagnetism of O₂

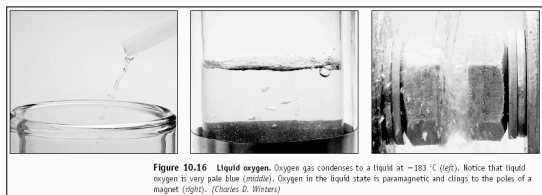


Figure 10.16 Liquid oxygen. Oxygen gas condenses to a liquid at -183°C (left), notice that liquid oxygen is very pale blue (middle). Oxygen in the liquid state is paramagnetic and clings to the poles of a magnet (right). (Charles D. Winters)

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Four Principles of MO Theory

Principle #1:

Number of Molecular Orbitals =
Number of Atomic Orbitals

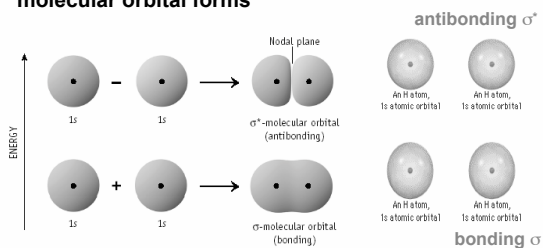
Two 1s orbitals from two hydrogen atoms create two molecular orbitals in H₂

Two 1s orbitals and two 2s orbitals from two lithium atoms create four molecular orbitals in Li₂

See *Four Principles of MO Handout*

Molecular Orbital Type

When two atomic 1s H orbitals combine, a bonding (σ) and antibonding (σ^*) molecular orbital forms



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Four Principles of MO Theory

Principle #2:

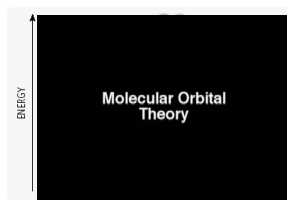
Bonding MO lower in energy than the parent orbital
Antibonding MO higher in energy than the parent orbital

Principle #3:

Electrons of molecule assigned to successively higher MOs

Use *Pauli Exclusion Principle* and *Hund's Rule* when assigning electrons

MO Diagram for H₂



Antibonding MO

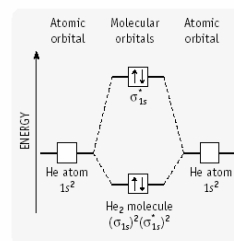
Atomic Orbitals

Bonding MO

Two 1s electrons from two H atoms occupy the σ orbital in H₂

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MO Diagram for He₂



Antibonding MO

Atomic Orbitals

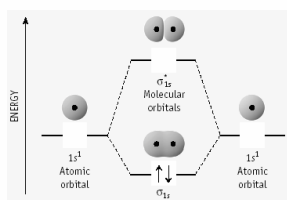
Bonding MO

Two 1s electrons in σ ,
Two 1s electrons in σ^*

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Bond Order in MO Theory

$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$



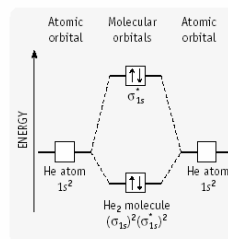
Bond Order > 0,
stable molecule
Bond Order = 0 or < 0,
unstable molecule

In H₂,
Bond Order =
 $\frac{1}{2}(2 - 0) = 1$;
stable

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Bond Order in MO Theory

$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$



Bond Order > 0,
stable molecule
Bond Order = 0 or < 0,
unstable molecule

In He₂,
Bond Order =
 $\frac{1}{2}(2 - 2) = 0$;
unstable

∴ He₂ does not exist

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Four Principles of MO Theory

Principle #4:

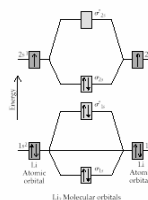
Atomic orbitals combine to give molecular orbitals only when the atomic orbitals are of similar energy

Similar energy = better overlap

- 1s + 1s = good MO
- 1s + 2s = poor MO
- 2s + 2s = good MO
- 2s + 2p = poor MO
- 3s + 2s = poor MO
- ... etc. ...

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Example: Dilithium, Li₂

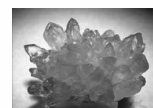


Note: no overlap between 1s and 2s

Bond Order = $\frac{1}{2}(4 - 2) = 1$

Stable molecule

Would you expect Be₂ to exist? Why?



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p orbitals and π bonds

Three possible p orbitals on each atom - *six total* p MO orbitals

Two p orbitals create 2 σ MO bonds

Four remaining p orbitals create 4 π MO bonds

Four p atomic orbitals create four π molecular orbitals,
 π = bonding (2)
 π^* = antibonding (2)

... but there's a catch!

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p orbitals and π bonds

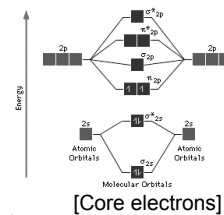
For B, C and N,

π orbitals lower energy than σ orbital

π^* orbitals lower energy than σ^* orbital

Example: B_2

Bond Order = 1



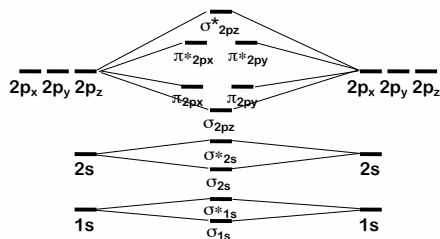
MAR See MO Diagram ($B_2 - N_2$) Handout

p orbitals and π bonds

For O, F and Ne,

σ orbital lower energy than π orbitals

π^* orbitals lower energy than σ^* orbital



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p orbitals and π bonds

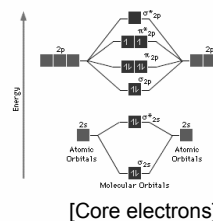
For O, F and Ne,

σ orbital lower energy than π orbitals

π^* orbitals lower energy than σ^* orbital

Example: O_2

Bond Order = 2

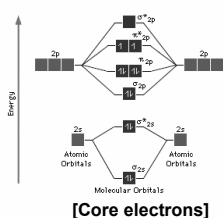


MAR See MO Diagram ($B_2 - N_2$) Handout

Paramagnetism

Paramagnetism exists when unpaired electrons in MO diagram

O_2 is paramagnetic; unpaired electrons in two π^* orbitals

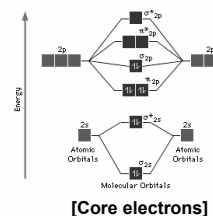


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Paramagnetism

Paramagnetism exists when unpaired electrons in MO diagram

N_2 is diamagnetic; all electrons paired

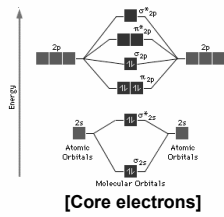


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Molecular Orbital Notation

Used to abbreviate the MO diagrams

- Ignore core electrons
- Write in order of increasing energy



For N₂:

$$[\text{core electrons}](\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$$

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Sigma and Pi Bonds

Determine sigma and pi bonds using:

$$\# \sigma \text{ bonds} = \frac{1}{2} (\# \sigma \text{ bonding e}^- - \# \sigma \text{ antibonding e}^-)$$

$$\# \pi \text{ bonds} = \frac{1}{2} (\# \pi \text{ bonding e}^- - \# \pi \text{ antibonding e}^-)$$

and

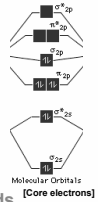
$$\# \sigma \text{ bonds} + \# \pi \text{ bonds} = \text{bond order}$$

For N₂: [core electrons](σ_{2s})²(σ*_{2s})²(π_{2p})⁴(σ_{2p})²

$$\# \sigma \text{ bonds} = \frac{1}{2}(4 - 2) = 1 \sigma \text{ bond}$$

$$\# \pi \text{ bonds} = \frac{1}{2}(4 - 0) = 2 \pi \text{ bonds}$$

$$\text{bond order} = \frac{1}{2}(8 - 2) = 3 = 1 \sigma + 2 \pi \text{ bonds}$$



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MO Diagram for Diatomics

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ* _{2p}	□	□	□	□	□	□
π* _{2p}	□	□	□	□	□	□
σ _{2p}	□	□	□	□	□	□
π _{2p}	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑
σ* _{2s}	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑
σ _{2s}	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	298	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Note: all should have [core electrons]

Changes in MO diagrams due to s-p mixing and/or electron repulsion

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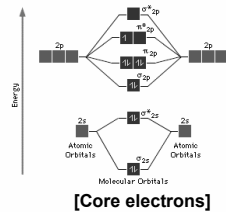
Ionic Diatomic Molecules

Predicting Ionic Diatomic MO diagrams simple
Use Hund and Pauli

Example: O₂⁺

Remove electron from π*_{2p} orbital

Check bond order, paramagnetism



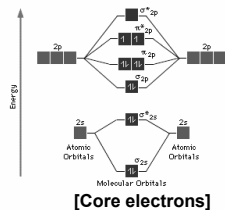
[Core electrons]

Ionic Diatomic Molecules

Predicting Ionic Diatomic MO diagrams simple
Use Hund and Pauli

Example: O₂⁻

Using the O₂ diagram on the right, where would you place the extra electron? Is O₂⁻ more or less stable than O₂? Why?



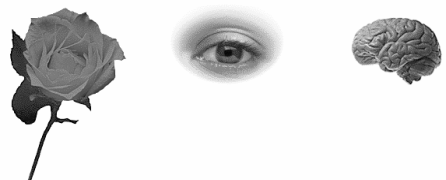
[Core electrons]

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Application: Vision

Molecular Orbital Theory helps to describe the process of vision - photochemistry



Application: Band Theory

In metallic bonding, electrons delocalized over metallic lattice - a sea of electrons

MO energies identical, excellent overlap

Helps explain conductivity, malleability, more



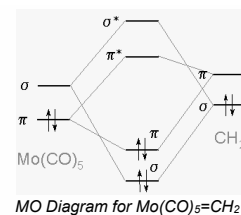
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End of Chapter 8

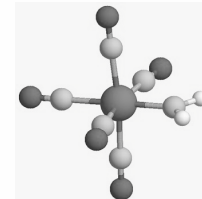
See:

- [Chapter Eight Study Guide](#)
- [Chapter Eight Concept Guide](#)
- [Important Equations \(following this slide\)](#)
- [End of Chapter Problems \(following this slide\)](#)

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MO Diagram for $\text{Mo}(\text{CO})_5=\text{CH}_2$



Important Equations, Constants, and Handouts from this Chapter:

- the bond order, bond energy and bond length relationships still apply to both theories
- know the advantages and disadvantages of the Valence Bond and Molecular Orbital theories
- see the Geometry and Polarity Guide and the two Molecular Orbital Theory diagrams (NBC and FONE) (handouts)

Valence Bond / Hybridization Theory: types of hybridization (sp, sp², etc.), sigma and pi bonds

Molecular Orbital Theory: bonding and antibonding orbitals, sigma bonds and pi bonds, paramagnetic and diamagnetic, the "NBC" vs. "FONE" diagrams

$$\text{bond order (MO theory)} = \frac{1}{2}(\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$

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End of Chapter Problems: **Test Yourself**

Be sure to view practice problem set #2 and self quizzes for MO theory and Valence Bond theory examples and practice

1. Specify the electron-pair and molecular geometry for each of the following. Describe the hybrid orbital set used by the central atom in each molecule or ion.
a. BBr₃ b. CO₂ c. CH₂Cl₂ d. XeF₄
2. Use MO theory to tell which has the largest bond order: C₂ or F₂. Are either species paramagnetic?
3. Use MO theory to speculate on the existence of dilithium.
4. Which compound is stronger by MO theory: Be₂ or B₂⁺.
5. Describe the hybridization change on carbon as methane (CH₄) is burned to create carbon dioxide.

End of Chapter Problems: **Answers**

1. a. trigonal planar, trigonal planar, sp². b. linear, linear, sp. c. tetrahedral, tetrahedral, sp³. d. octahedral, square planar, sp³d²
2. BO(C₂) = 2, diamagnetic. BO(F₂) = 1, diamagnetic.
3. By MO theory, dilithium (Li₂) should exist (BO = 1, diamagnetic.)
4. MO theory would predict that B₂⁺ (bond order = 0.5, paramagnetic) is stronger than Be₂ (bond order = 0, this should not exist at all.)
5. sp³ to sp

Be sure to view practice problem set #2 and self quizzes for MO theory and Valence Bond theory examples and practice

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